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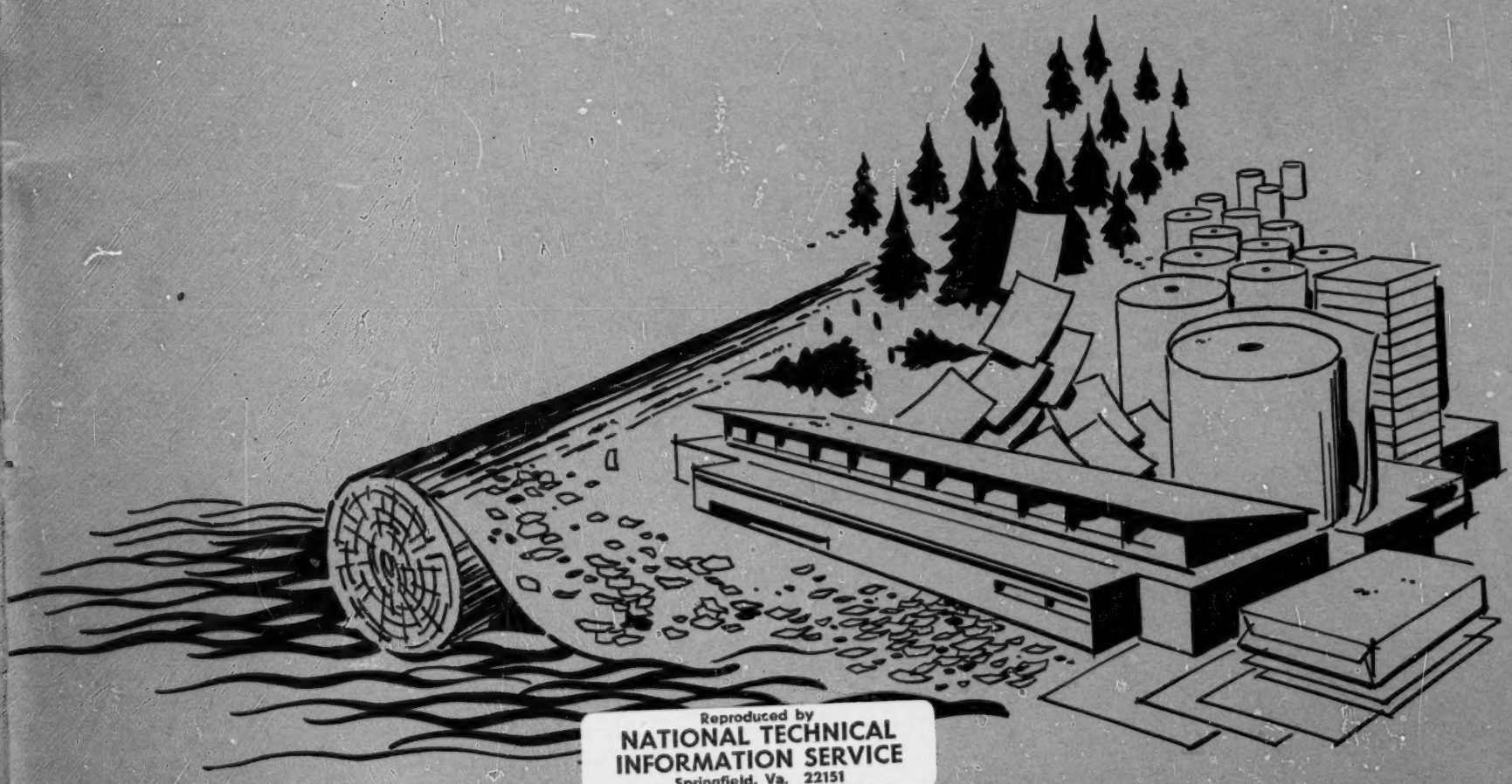
Pollution Abatement by Fiber Modification



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27 Abstract

Laboratory studies were conducted to determine if the collection of pollutants from water using fibers was a feasible concept. Any cellulosic or lignocellulosic fibers can be reacted with di- or tri-halogeno-s-triazines in simple aqueous conditions so that about 10% by weight of reactive sites can be built into the fiber. The modified fibers can be regarded as polychloro-s-triazinylated fibers in which each s-triazine ring contains approximately one or two reactive chlorine atoms. The extent of reaction is generally determined by the stereotopochemistry of the fiber and in particular by its lignin content and its microporous structure. Chloro-s-triazines are capable of reacting in aqueous solutions with amines, mercaptans and phenols, typical of those present in pulping wastes and bleach plant effluent. The efficiency of this system is obviously increased as the size of the pollutant removed per reactive fiber size is increased. Methods to increase the size of lignosulfonates by condensation have therefore been developed.

Two new methods for the collection of pollutants by fibers based on oxidative grafting and physical entrapment by hydrodynamic volume changes have also been discovered and a procedure for the characterization of copolymer compositions by surface tension has been established. (EPA abstract)

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POLLUTION ABATEMENT BY FIBER MODIFICATION

by

Institute of Forest Products
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a report for the
Environmental Protection Agency

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January 1971

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ABSTRACT

Laboratory studies were conducted to determine if the collection of pollutants from water using fibers was a feasible concept.

Any cellulosic or lignocellulosic fibers can be reacted with di- or tri-halogeno-s-triazines in simple aqueous conditions so that about 10% by weight of reactive sites can be built into the fiber. The modified fibers can be regarded as polychloro-s-triazinylated fibers in which each s-triazine ring contains approximately one or two reactive chlorine atoms. The extent of reaction is generally determined by the stereotopochemistry of the fiber and in particular by its lignin content and its microporous structure. Chloro-s-triazines are capable of reacting in aqueous solutions with amines, mercaptans and phenols, typical of those present in pulping wastes and bleach plant effluent. The efficiency of this system is obviously increased as the size of the pollutant removed per reactive fiber size is increased. Methods to increase the size of lignosulfonates by condensation have therefore been developed.

Two new methods for the collection of pollutants by fibers based on oxidative grafting and physical entrapment by hydrodynamic volume changes have also been discovered and a procedure for the characterization of copolymer compositions by surface tension has been established.

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CONCLUSIONS

1. Water pollutants consisting of amines, mercaptans and phenols can be removed from solution by three methods of entrapment on or within fibers.

2. Of these, fiber modification by halogeno-s-triazines is the most general and technically flexible procedure for pollutant entrapment.

3. From a technical and economic standpoint the most attractive procedure for the removal of lignosulfonates from spent sulfite waste liquor will probably be based on their oxidative grafting to lignocellulosic fiber sheets for the improvement of strength properties.

4. The oxidative grafting procedures using lignocellulosic fibers offer promise as a general means of removing low concentrations of phenolic pollutants from water. Thus, this research is of potential importance for three main reasons:

   (a) New methods for modifying lignocellulose fiber surfaces have been developed which, with further work, may be industrially acceptable within the framework of existing papermaking practices.

   (b) The modified fibers may extend the range of utility of lignocellulosic fiber and lead to paper products with improved rigidity when wet.

   (c) If these improvements can be achieved using the materials present in discharged pulp liquors it should reduce river and stream pollution both by providing a large volume outlet for this waste and the incentive to attempt to utilize it.

RECOMMENDATIONS

1. Research in the area of pollution abatement by fiber modification should be continued.

2. Emphasis in future research should be placed on the development of a viable process suitable for a pilot demonstration project.

3. Such a process should focus on the change in the strength properties of groundwood fiber sheets caused by the grafting of lignosulfonates from spent sulfite waste liquor.

INTRODUCTION

Wood is a natural fiber composite consisting of approximately 60% polysaccharide and 30% polyphenolic macromolecules. For many uses, the pulp and paper industry separates the polysaccharide material as fibers and simultaneously generates water soluble derivatives of the natural insoluble phenolic polymer of the tree. It is important to appreciate the tremendous quantities of these lignin derivatives available because thus far only relatively minor uses for this polymer have been discovered. In effect, there is roughly one pound of these pulp wastes for every two pounds of paper, and the U. S. production of paper in 1969 was approximately 50 million tons. The phenolic material can broadly be divided into two categories; kraft lignin and lignosulfonates. The former is the larger nationally and originates from the kraft pulping process. The lignosulfonates on the other hand are predominant in the Pacific Northwest where some of the world's largest sulfite mills are located. Washington has approximately 32 pulp mills and these are large in size. Immense quantities of lignosulfonates are therefore generated and discharged into the waterways of the Pacific Northwest. Kraft lignin can be disposed of by burning and does not constitute an intrinsic water quality hazard although this is a poor use of a polymer carefully grown and protected for more than half a century. Nonetheless, kraft lignin may end up in part as a water pollutant since it is not completely removed from the fiber during pulping and if the pulp is subsequently bleached a bleach plant effluent is created. Washington and Oregon also contain about 16 kraft mills which generate quantities of bleach plant effluent. This may contain chlorinated phenolic material toxic to aquatic life and derived from the residual lignin of the fiber. The lignosulfonates however are much larger volume water pollutants as their historical disposal has been simple dumping in streams, rivers and waterways. This is manifestly undesirable, for in addition to their water polluting qualities per se, lignosulfonates function as dispersants maintaining solid material in suspension which would otherwise settle out.

It is therefore a worthwhile research goal to develop systems capable of abating the pollution resulting from the discharge of lignosulfonates or bleach plant effluent into the waters of the Pacific Northwest by finding a suitable use for these pollutants. However, because of the quantity of material in question there are relatively few uses which can be seriously envisaged. The underlying concept of this work has been that wood fiber composites themselves provide one such use opportunity by virtue of their volume and intimate commercial connection with the production of the pollutants. More specifically, the ultimate goal has been to devise procedures for the attachment of lignosulfonates or other lignin-derived pollutants to wood or pulp fibers to create useful fiber-polymer composites.

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DISCUSSION OF RESULTS

The original broad aims of this program were:

(1) to determine what species, size and shape of molecule can be attached to lignocellulosic fibers using simple reactions compatible with the established processes for the manufacture of fibrous products;

(2) to investigate the effect of the attachment of such molecules on the physical properties of fibers and fiber composites, and

(3) to use this information to assess the feasibility of reducing water pollution due to pulp liquor discharge by reattaching the waste polymeric chemicals contained therein to paper and wood fibers.

In the pursuit of these goals a number of technical and economic constraints have to be recognized from the outset. These include:

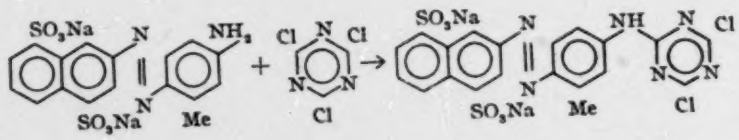
(a) The procedure for the attachment of the pollutants to the fiber must be capable of being carried out in an aqueous medium preferably at ambient temperatures and in a pH range close to neutral,

(b) A relatively substantial amount of pollutant needs to be attached per unit of fiber.

(c) The anticipated properties of the final fiber-pollutant composite will indicate applications such as shipping containers where strength and rigidity (but not whiteness) are important.

Attention was therefore initially directed towards gaining an understanding of the chemistry involved in the attachment of phenolic materials to fiber surfaces.

The original plan was predicated upon the then unrecognized potential of fiber reactive dye chemistry as a general foundation for fiber modification. The act of dyeing is, after all, a chemical modification and it seemed entirely rational to build up on the thousands of man-years of research which had culminated in the development of fiber reactive dyes in 1956. These dyes are known to form covalent bonds with cellulosic fibers at ambient temperatures and at pH values between 10 and 11 by the reaction depicted in equation (1).



Preparation of dye.

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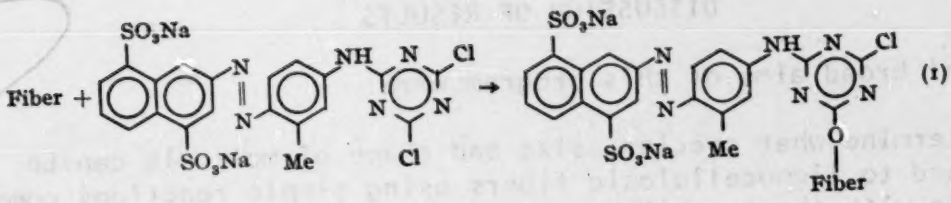

(1)

Reaction with fiber.

The long unperceived key to the selective reaction of dye with the hydroxyl groups of the fiber rather than the infinitely more numerous hydroxyl groups of the water resides in a combination of simple physico-chemical facts. Thus, firstly, it is the hydroxyl and cellulosate anions which are in competition for the modifying species, not the water and cellulose hydroxyls and the latter are substantially in excess within the pH range 7-12. Second, the rate of reaction of the modifying species with the fiber is determined by its concentration in the fiber phase and not by its much lower concentration in the surrounding water.

→ The report describes research

Our first task therefore was to determine whether the chemistry developed for dyeing cotton was applicable to wood derived fibers of differing morphology and chemical composition. A typical dichloro-s-triazine fiber reactive dye was selected because of its availability and because after reaction it would still be expected to contain one reactive chlorine suitable for the attachment of pollutants. This The dye was found to smoothly react with a wide variety of wood-derived fibers in amounts theoretically suitable for the subsequent attachment of substantial amounts of lignosulfonates or bleach plant effluents. The effects of various reaction conditions including pH and time, were investigated and are summarized in Figs. 1-8.

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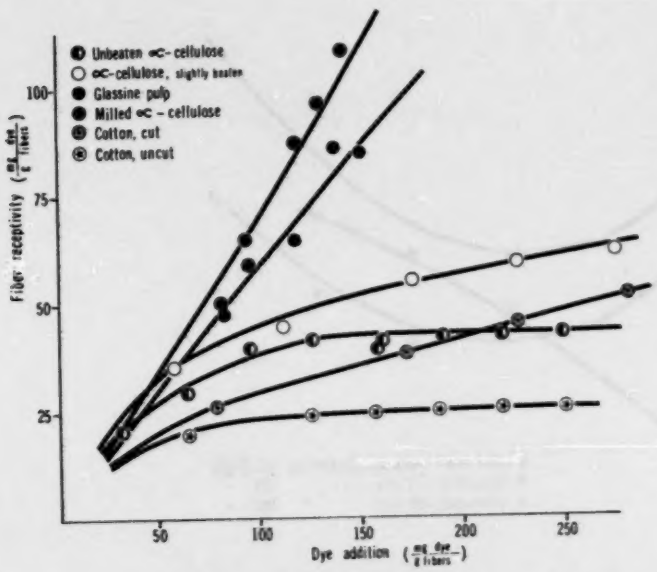


Fig. 1. Dye receptivity of papermaking fibers.

Fig 1 shows the fiber reactive dye receptivity (in mg dye/g fiber) of cellulosic fibers at various dye addition levels, and shows that beyond a certain value the addition of further dye is without effect on the receptivity.

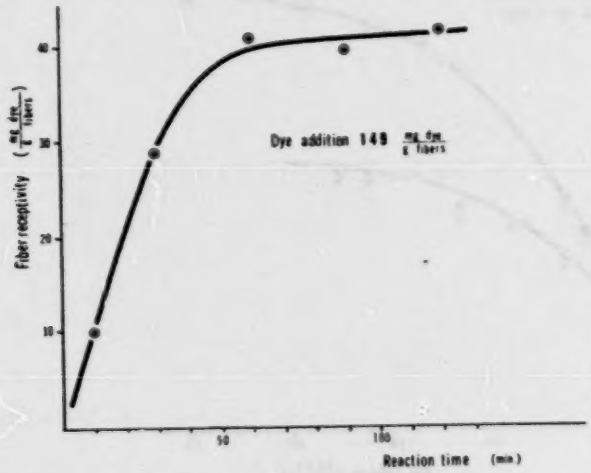


Fig. 2. Dye receptivity of unbeaten α-cellulose as function of reaction time.

Fig 2 shows the effect of reaction time on dye receptivity, and as in Fig 1, shows that beyond a certain level, here about 50 min, extended reaction times have little effect.

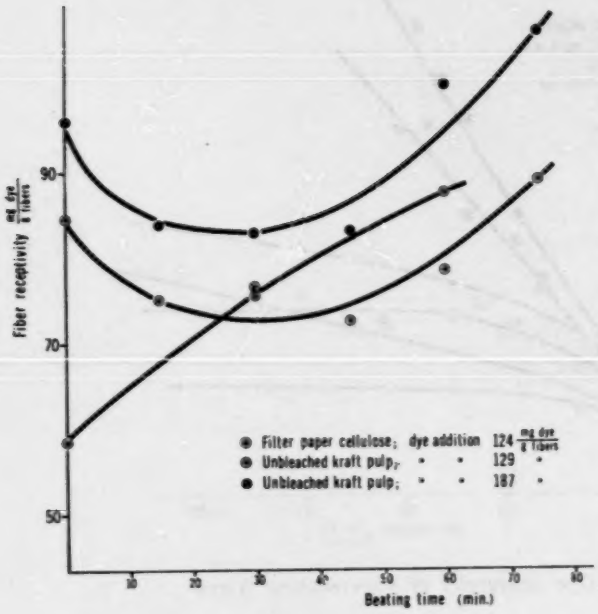


Fig. 3. Effect of beating on fiber receptivity.

Fig 3 shows the effect of beating upon the fiber receptivity, and as might be expected, the creation of new surfaces due to beating produces an increase in dye receptivity.

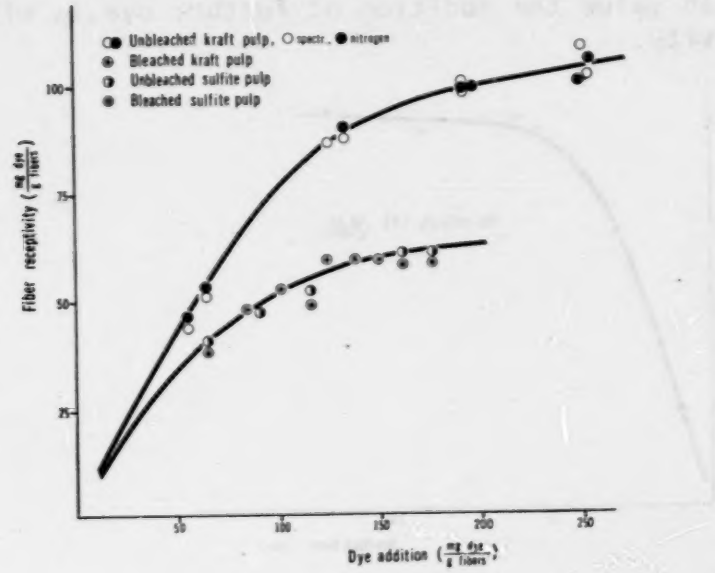


Fig. 4. Effect of bleaching on fiber receptivity.

Fig 4 shows the effect of bleaching upon the dye receptivity, and indicates that lignin reacts with the dye. It was further found that removal of the lignin from the fibers reduces dye receptivity to the level found for pure α-cellulose.

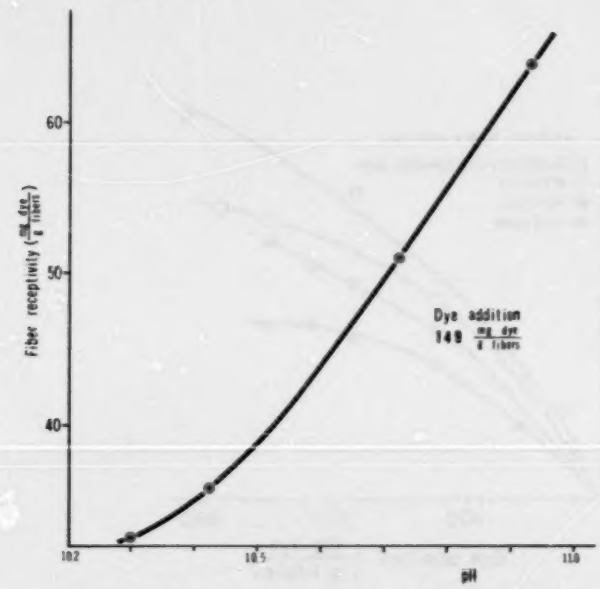
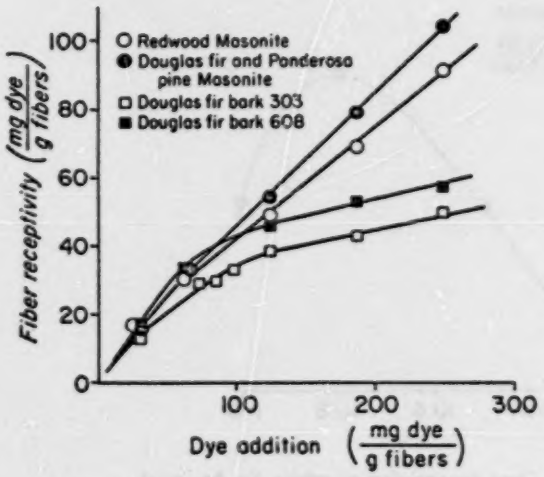


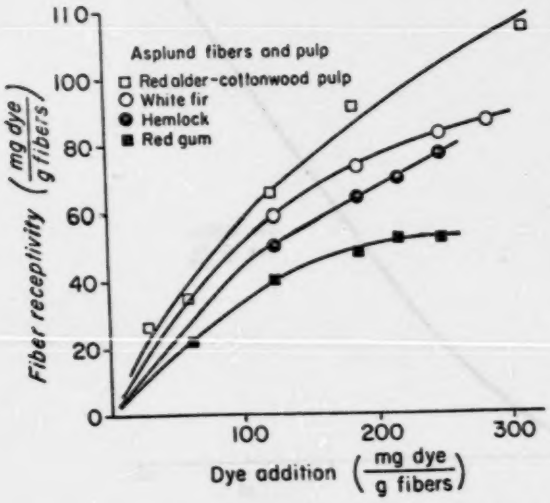
Fig. 5. Effect of pH on dye receptivity of unbeaten α-cellulose.

Fig 5 shows the effect of pH on the dye receptivity of α-cellulose, and shows the expected increase with pH as the concentration of cellulosate ion increases over this range.



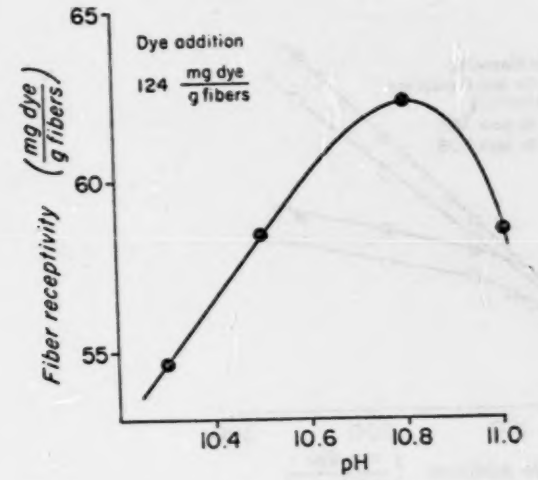
Dye receptivity of Masonite fibers and bark pulps

Fig 6 shows the dye receptivity of both Masonite fibers and bark pulps, which are seen to be similar to the results obtained in Fig 1.



Dye receptivity of Asplund whole wood fibers and Asplund pulp

Fig 7 shows the dye receptivity of Asplund fibers, and is seen to be similar to Figs. 1 and 6.



Effect of pH on fiber receptivity of white fir Asplund whole wood fibers

Fig 8 shows the dye receptivity of Asplund fibers, as a function of pH, and although similar to that in Fig 5 at pH less than 10.8, shows an unexpected drop at pH 11.

The important conclusion emerging from this phase of the research is that any wood fiber can be easily modified in water suspension at ambient temperatures so that 10% by weight of reactive sites can be introduced onto the fiber, which corresponds to some 10^{20} reactive sites per gram of fiber. The presence of the reactive sites was shown by neutron activation analysis using the Nuclear Reactor facilities of the University of Washington. The speed and facility of this method of the analysis of fibers have made a tremendous contribution to the rate of progress of this investigation and the technical assistance of Dr. G. L. Woodruff and Mr. W. P. Miller and the administrative cooperation of Professor A. Babb are gratefully and explicitly acknowledged.

With the means of activating any wood fiber now in hand, attention was turned to a study of the reactivity of these fibers towards the phenolic pollutants. To establish the basic reaction conditions some model experiments were first undertaken. These employed cyanuric chloride as a model for the chloro-s-triazinylated fiber and monomeric phenols with various substituents, selected to simulate the structural environments of the phenolic hydroxyl groups in lignosulfonates and bleach plant effluent. Since the lignin hydroxyl groups are often flanked by substituents in the 2 and 6 positions, reaction with cyanuric chloride is difficult or impossible if the substituent groups are too large, and the results in Table I illustrate this. In the case of lignin and pulp wastes there may possibly be even greater steric hindrance than in the case of the model compounds.

General Reaction Scheme

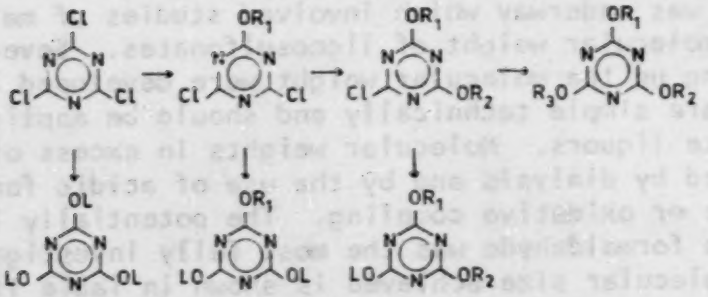


TABLE I

Monomeric Phenols Used as Models to Simulate the Reactivity of Phenolic Hydroxyl Groups in Lignins and Bleach Plant Effluents

Unreactive Phenols

2-t-butyl-
2-benzoyl-4-dodecyloxy -
2-methoxy-4-formyl-6-nitro -
4-t-butyl-2-phenyl-

Phenols Giving Di-substituted Products

4-aceto-2-methoxy -
2-chloro-4-phenyl -
2,6-dimethoxy -
2,6-dimethyl -

Phenols Giving Tri-substituted Products

4-sec-amyl-
3-benzoxy-
2-benzyl-4-chloro-
4-bromo-
4-t-butyl-
5-chloro-2-formyl-
4-formyl-2-methoxy-
2-isopropyl-5-methyl-
3-isopropyl-
2-methoxy-
4-methoxy-
4-methylthio-3-methyl-
4-methylthio-
4-phenoxy-
8-quinolinoxy-

The results of this phase of the program gave the products described in Table II and defined steric problems and established the reaction conditions necessary for the combination of pollutants with cyanuric chloride.

Concurrently with these two phases of this investigation a separate research program was underway which involved studies of methods of controlling the molecular weight of lignosulfonates. Several techniques of building up the molecular weight were developed in this program. These are simple technically and should be applicable to sulfite pulp waste liquors. Molecular weights in excess of one million were achieved by dialysis and by the use of acidic formaldehyde, cyanuric chloride or oxidative coupling. The potentially low cost condensation with formaldehyde was the most fully investigated and the control of molecular size achieved is shown in Table III.

TABLE II

The products obtained from the reaction of phenolic hydroxyl groups in various environments with cyanuric chloride

Characteristics of aryloxy-*s*-triazines.

Compound	Crystalline form	M.p. °C	Yield Wt.	Yield %	Formula	M.W.	Carbon % Calc.	Carbon % Found	Hydrogen % Calc.	Hydrogen % Found	Nitrogen % Calc.	Nitrogen % Found
2,4,6-Tri(4-*sec*-amylphenoxy)-*s*-triazine	blades [a,c]	183–184	6.7 g	59	$C_{36}H_{45}N_3O_3$	567.8	76.15	75.96	7.99	7.8	7.40	7.9
2,4,6-Tri(3-benzoxyphenoxy)-*s*-triazine	felted needles [a]	187–189	10.5	75	$C_{42}H_{27}N_3O_9$	717.7	70.28	70.33	3.79	4.0	5.85	5.9
2,4,6-Tri(2-benzyl-4-chlorophenoxy)-*s*-triazine	fine nodules [e]	144–145	4.0	55	$C_{42}H_{30}N_3O_3Cl_3$	731.1					5.75	6.0
2,4,6-Tri(4-bromophenoxy)-*s*-triazine *	thin strands [a]	130–131	5.0	84	$C_{21}H_{12}N_3O_3Br_3$	594.1	42.44	42.71	2.04	2.0	7.07	7.3
2,4,6-Tri(4-*t*-butylphenoxy)-*s*-triazine	spiky needles [a,c]	191–193	4.1	40	$C_{33}H_{39}N_3O_3$	525.7	75.39	75.36	7.48	7.7	7.99	8.1
2,4,6-Tri(5-chloro-2-formylphenoxy)-*s*-triazine	soft needles [d]	176–177	1.8	30	$C_{24}H_{12}N_3O_6Cl_3$	544.7	52.90	52.75	2.22	2.4	7.71	7.9
2,4,6-Tri(4-formyl-2-methoxyphenoxy)-*s*-triazine	hard nodules [b]	208–210	7.5	70	$C_{27}H_{21}N_3O_9$	531.5					7.91	7.9
2,4,6-Tri(2-isopropyl-5-methylphenoxy)-*s*-triazine **	rhombohedrons [a]	158–160	3.8	36	$C_{33}H_{39}N_3O_3$	525.7					7.99	8.0
2,4,6-Tri(3-isopropylphenoxy)-*s*-triazine	fine needles [a]	130–132	5.0	52	$C_{30}H_{33}N_3O_3$	483.6					8.69	8.9
2,4,6-Tri(2-methoxyphenoxy)-*s*-triazine	rhombohedrons [a]	164–166	4.2	94	$C_{24}H_{21}N_3O_6$	447.5	64.43	63.83	4.73	4.9	9.39	9.3
2,4,6-Tri(4-methoxyphenoxy)-*s*-triazine	felted needles [a]	199–200	4.2	94	$C_{24}H_{21}N_3O_6$	447.5	64.43	64.21	4.73	4.8	9.39	9.4
2,4,6-Tri(4-methylthio-3-methylphenoxy)-*s*-triazine	blades [f]	237–238	5.5	51	$C_{27}H_{27}N_3O_3S_3$	537.7					7.81	7.5
2,4,6-Tri(4-methylthiophenoxy)-*s*-triazine	felted needles [a]	216–217	8.1	81	$C_{24}H_{21}N_3O_3S_3$	495.7					8.48	8.4
2,4,6-Tri(4-phenoxyphenoxy)-*s*-triazine	fine needles [a]	219–221	2.5	40	$C_{39}H_{27}N_3O_6$	633.7	73.93	73.66	4.30	4.2	6.63	6.6
2,4,6-Tri(8-quinolinoxy)-*s*-triazine	fine prisms [a,b]	260–262	2.8	55	$C_{30}H_{18}N_6O_3$	510.5	70.58	70.71	3.55	3.8	16.46	16.7
2-Chloro-4,6-di(4-aceto-2-methoxyphenoxy)-*s*-triazine#[2]	hard nodules [f]	204–205	5.3	61	$C_{21}H_{18}N_3O_6Cl$	443.9					9.47	9.3
2-Chloro-4,6-di(2-chloro-4-phenylphenoxy)-*s*-triazine#[1]	hard nodules [a]	188–190	2.8	41	$C_{27}H_{16}N_3O_2Cl_3$	520.8	62.26	62.31	3.10	3.1	8.07	8.2
2-Chloro-4,6-di(2,6-dimethoxyphenoxy)-*s*-triazine#[3]	prisms [a]	195–197	8.0	93	$C_{19}H_{15}N_3O_6Cl$	419.8					10.02	9.9
2-Chloro-4,6-di(2,6-dimethylphenoxy)-*s*-triazine#[4]	fine needles [g]	163–165	6.8	94	$C_{19}H_{18}N_3O_2Cl$	355.8					11.81	11.8

Crystallization solvents: [a] ethyl acetate, [b] dimethylformamide, [c] methanol, [d] hexane, [e] acetone, [f] dioxan, [g] ethanol.

* Bromine content; calc. 40.26 %, found 39.8 %.

(#1,2,3,4,) Chlorine content: (1) calc. 20.4 %, found 19.7 %; (2) calc. 8.0 %, found 7.8 %; (3) calc. 8.4 %, found 8.2 %; (4) calc. 10.0 %, found 10.5 %.

** Otto [21] gives m.p. 151° for this compound prepared by the fusion of cyanuric chloride and thymol.

TABLE III

Modification of Ammonium and Sodium Lignosulfonates by Dialysis and/or Condensation with Formaldehyde.

Lignosulfonate starting material	Duration of dialysis	Intrinsic viscosity after dialysis	Duration of condensation with formaldehyde	Intrinsic viscosity after condensation
Marasperse N-22	12 days	0.051 dl/g	0 hr	---- dl/g
Orzan A	15	0.057	11	0.078
Orzan A	15	0.057	20	0.097
Marasperse N-22	0	.036	60	0.013
Marasperse N-22	18	0.051	16	0.146
Orzan A	15	0.057	28	0.182
Orzan A	15	0.057	43	0.238
Marasperse N-22	18	0.051	29	0.303
Orzan A	15	0.057	48	0.385
Marasperse N-22	12	0.051	48	0.47

Table III shows the treatments used in the modification of lignosulfonated and the intrinsic viscosities of the modified products, both after dialysis and after further reaction with formaldehyde.

However, attempts to attach phenolic material to the reactive dyed fibers by means of the chlorine containing dye moiety were unsuccessful. This failure was shown to be caused by the presence of the negatively charged sulfonate groups on the dye which effectively repelled any approaching negatively charged phenolic material. Positively charged material, exemplified by amines on the other hand, was readily trapped by covalent attachment to the fiber. The amines used are listed in Table IV; and the effect of pH on the efficiency of their entrapment is illustrated by the data in Figs. 9-11.

TABLE IV

Amino Compounds Reacted with Dyed Fibers

Aromatic Amines	Other Amino Compounds
m-phenylene diamine	urea
m-aminophenol	melamine
p-aminophenol	
s-triaminobenzene	

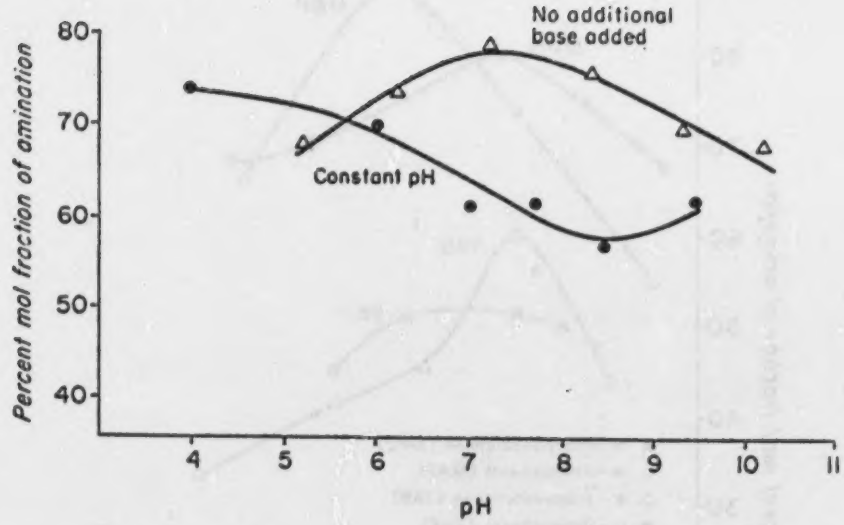


Fig 9 shows the effect of the reaction pH upon the reaction efficiency, and indicates that there is a maximum when the system is allowed to become self-buffering.

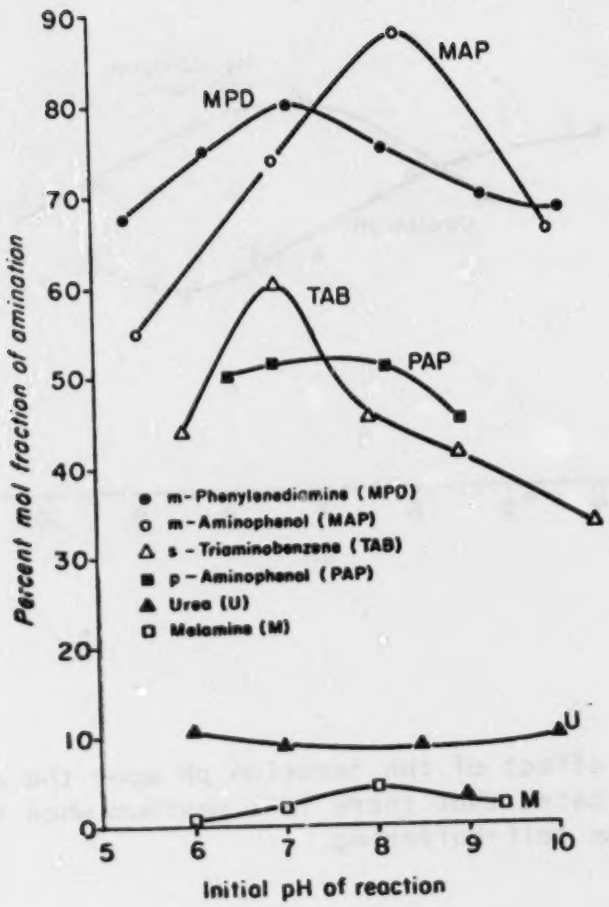
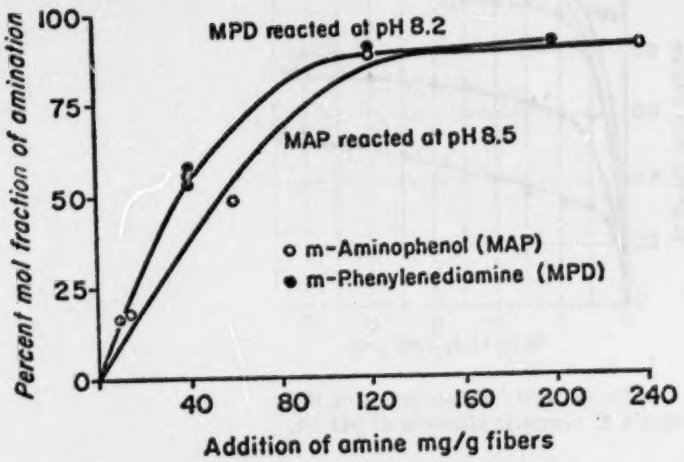


Fig 10 shows the effect of reaction pH on the efficiency of reaction, and shows that in most cases there is an optimum pH for greatest reaction efficiency.



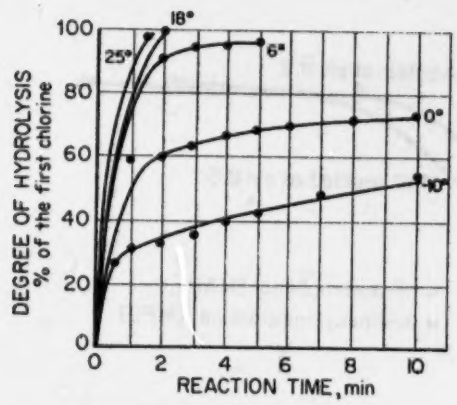
Efficiency of amination of chloro-s-triazinyl fibers by m-phenylenediamine and m-aminophenol.

Fig 11 shows the effect of amine concentration on the reaction efficiency, and indicates, as in Figs. 1 and 2, that there is a maximum beyond which further addition is pointless.

Thus the dyed fibers could perhaps be developed into an effective process for removing amine-containing impurities from water.

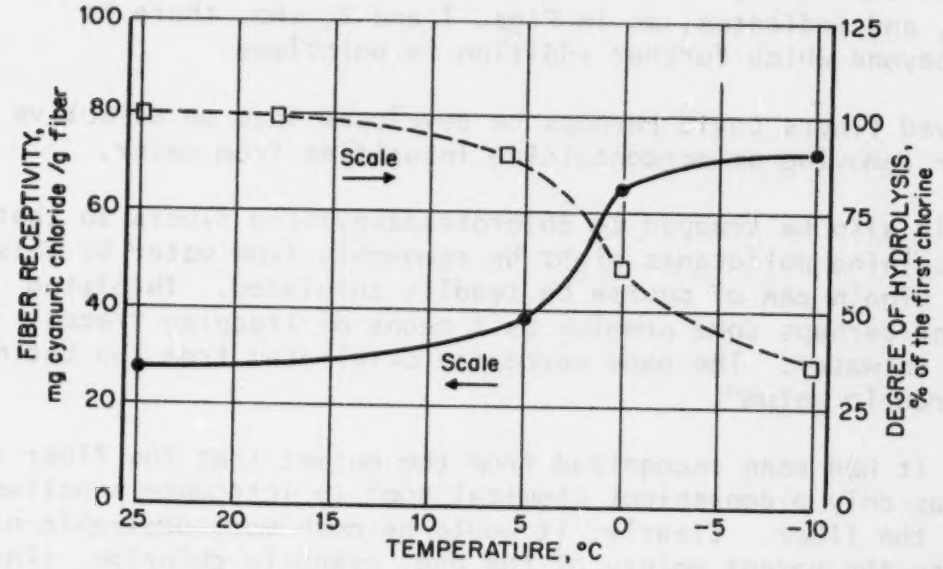
Thiols could also be trapped by chlorotriazinylated fibers so that sulfur-containing pollutants might be removable from water by this approach. Lignin can of course be readily thiolated. Thiolated fibers offer perhaps some promise as a means of trapping traces of mercury in water. The name mercaptan originates from the Latin "corpus mercurio aptum".

Of course, it had been recognized from the outset that the fiber reactive dye was only a convenient chemical tool to introduce reactive sites onto the fiber. Clearly, it would be much more desirable ultimately to use the parent moiety of the dye, cyanuric chloride, since it is a bulk chemical of commerce. Moreover, it contains three reactive sites and no unnecessary and unwanted dye moiety. An examination of the reaction of cyanuric chloride with wood fibers was therefore undertaken. By the use of a buffer system and a low temperature an unexpectedly extensive and extremely rapid reaction with fibers could be achieved as exemplified by the data in Figs. 12-16 and Tables V-IX.



Temperature dependence of the hydrolysis of cyanuric chloride at pH 10.

Fig 12 shows the temperature dependence of the hydrolysis of cyanuric chloride at pH 10, and indicates a drastic drop in hydrolysis with a drop in temperature.



Temperature dependence of fiber receptivity vs. hydrolysis of cyanuric chloride.

Fig 13 shows the effect of temperature on fiber receptivity, which is seen to increase with decreasing temperature, presumably as a result of the decrease in hydrolysis.

TABLE V

Effect of Temperature on Fiber Receptivity

(which is seen to increase with decreasing temperature, presumably due to the decrease in hydrolysis)

Effect of Temperature on Fiber Receptivity

Reaction Procedure "A"

Temperature, °C	*Reaction time, min*	*Nitrogen content of fibers, mg/g*	*Cyanuric chloride reacted with fibers, mg/g*	*No. of chlorine atoms per s-triazine ring*
25	10	6.3	27.6	
5	7	8.6	38.0	0.51
0	7	14.7	64.5	
−10	7	16.4	71.9	1.44

TABLE VI

Effect of Reaction Time on Fiber Receptivity

Effect of Reaction Time on Fiber Receptivity

Reaction Procedure "B," with addition of 1*N* NaOH (12.5 ml)

Reaction time, min	*Nitrogen content of fibers, mg/g*	*Cyanuric chloride reacted with fibers, mg/g*	*Chlorine content of fibers, mg/g*	*No. of chlorine atoms per s-triazine ring*
1	12.8	56.2	15.6	1.36
5	13.6	59.8	16.5	1.44
10	15.8	69.0	18.8	1.42

TABLE VII

Effect of Cyanuric Chloride Concentration on Fiber Receptivity

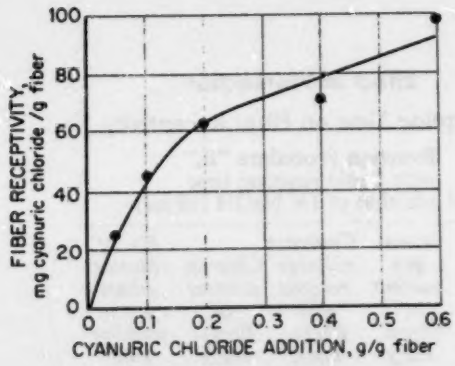
(which may be seen graphically in Figure 14)

Effect of Cyanuric Chloride Concentration on Fiber Receptivity

Reaction Procedure "B"

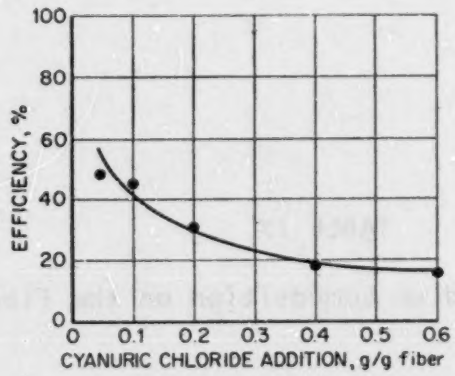
Alkali addition 1N NaOH, ml	*Nitrogen content of fibers, mg/g*	*Cyanuric chloride reacted with fibers, mg/g*	*Chlorine content of fibers, mg/g*	*No. of chlorine atoms per s-triazine ring*
50 mg cyanuric chloride added per 1 g fiber				
1.0	4.7	20.6	6.1	1.54
2.0	5.6	24.6	8.2	1.73
3.5	5.4	23.7	...	...
8.0	5.5	24.1	...	...
100 mg cyanuric chloride added per 1 g fiber				
1.0	5.0	21.9	...	...
2.5	6.9	30.3	...	...
3.5	7.3	32.0	12.7	2.0
5.0	9.5	41.7	9.9	1.23
7.5	10.3	45.2	8.2	1.00
10.0	7.7	33.8	...	...
200 mg cyanuric chloride added per 1 g fiber				
2.5	7.5	32.9	7.5	1.19[a]
5.0	9.2	40.4	9.4	1.20[a]
7.5	13.6	59.6	12.2	1.07[a]
10.0	14.2	62.3	...	...
400 mg cyanuric chloride added per 1 g fiber				
5.0	7.4	32.5	1.11	1.86
12.5	13.9	61.0	...	...
15.0	15.7	68.9	20.4	1.55
25.0	16.2	71.0	18.0	1.30
600 mg cyanuric chloride added per 1 g fiber				
15.0	17.2	75.5	19.3	1.33[b]
20.0	20.4	89.5	...	...
25.0	22.2	97.4	26.5	1.42[b]
30.0[c]	24.7	108.5	...	...
40.0[c]	20.9	91.8	...	...

[a] Dried at 110°, 24 hr.
[b] Dried at 110°, 5 hr.
[c] Addition time, 2.5 min.



Effect of cyanuric chloride concentration on fiber receptivity.

Fig 14 shows the effect of cyanuric chloride concentration on the receptivity, and is similar to that in Fig 1.



Efficiency of the reaction of cyanuric chloride with kraft fibers.

Fig 15 shows the efficiency of reaction of cyanuric chloride with kraft fibers as a function of the amount of cyanuric chloride added per gram of fiber, and indicates an almost linear relationship between efficiency and cyanuric chloride addition.

TABLE VIII

Effect of the Pre-reaction Adsorption Time on Fiber Receptivity'

Effect of Prereaction Adsorption Time on Fiber Receptivity

Reaction Procedure "B," with 1 min reaction time and addition of 1*N* NaOH (10 ml)

Adsorption time, min	*Nitrogen content of fibers, mg/g*	*Cyanuric chloride reacted with fibers, mg/g*	*Chlorine content of fibers, mg/g*	*No. of chlorine atoms per s-triazine ring*
0	9.1	39.7	11.0	1.44
2	10.0	43.7		
10	9.9	43.5	11.4	1.36
15	10.8	47.5	10.7	1.17

Here the fiber suspension and cyanuric chloride are mixed for the stated adsorption time prior to the addition of base to start the reaction.

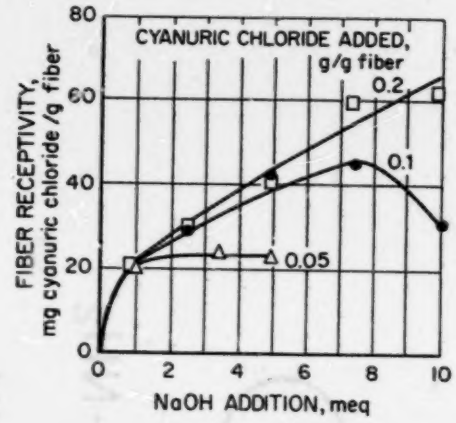
TABLE IX

Effect of the Reaction Medium Composition on the Fiber Receptivity

Effect of Acetone/Water Ratio on Fiber Receptivity

Reaction Procedure "B," with addition of 0.2 g of cyanuric chloride per 1 g fibers and 1*N* NaOH (6 ml).

Acetone content of mixture, %	*Nitrogen content of fibers, mg/g*	*Cyanuric chloride reacted with fibers, mg/g*	*Chlorine content of fibers, mg/g*	*No. of chlorine atoms/s-triazine ring*
60	11.5	50.7	14.5	1.49
80	12.2	53.5	15.3	1.49
100	13.5	61.9	15.0	1.27



Fiber receptivity vs. NaOH addition.

Figure 16 shows the effect of the amount of base added on the fiber receptivity for various cyanuric chloride to fiber ratios.

This theoretically should yield a dichloro-s-triazinylated fiber since only one of the original three chlorines has been used to attach the s-triazine ring to the fiber. However, some additional chlorine atoms are dissipated hydrolytically or in inter-chain crosslinking and each s-triazine ring attached to the fiber therefore contains on the average about 1.5 reactive site per s-triazine ring. These reactive chlorine atoms are capable of reacting with phenolic, amino and also thiol groups.

The research therefore had now reached the point where aqueous reaction conditions had been established for the proposed attachment of phenolic impurities to wood fibers using a cyanuric chloride bridge.

However, very little could be said about the points of attachment of pollutant to be preferred from a strength point of view. The preferred size of the pollutant to be attached to the fiber was likewise obscure. To clarify these points some knowledge of the topography of the fibers was needed and it was fortunate that a major contribution to this area was forthcoming during the period covered by this grant. Thus, Stone and Scallan, using a series of polysaccharides as molecular probes, were able to show that typical pulp fibers have a multilamellar microporous cell wall. Although their views may not be correct in every detail, the concept is certainly applicable to the problem of attaching macromolecules to fibers. That is, very large macromolecules cannot penetrate into the smaller pores of the fiber and are thus located on the geometrical exterior of the fiber. Smaller molecules on the other hand can penetrate and later crosslink the interior of the cell wall. The general validity of these views was assessed by using a series of polyethylenimine polymers of known molecular weight. Polymerization of the monomer ethylenimine under acidic conditions

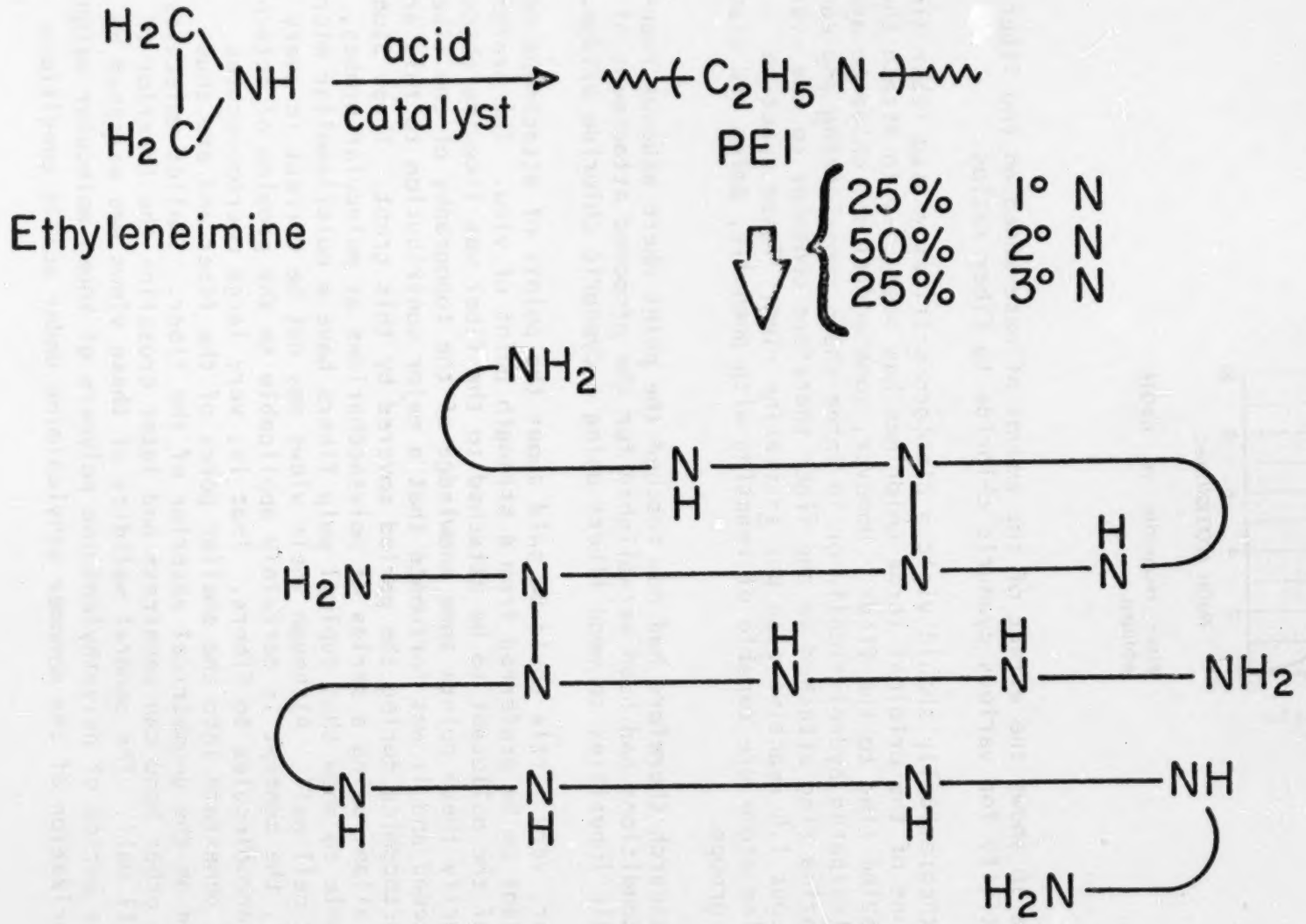


Fig 17. Preparation and structure of polyethylenimine.

(Fig 17) leads to a three dimensional network of amino nitrogen atoms which can assume a positive charge, become cationic in neutral or mildly acidic solution and thus are substantive to the naturally anionic cellulose macromolecules. The varied molecular weights and physical characteristics of the molecules used are shown in Table X.

Fig 17 shows the preparation and structure of polyethylenimine.

TABLE X

The Chemical and Physical Properties of the Polyamines Used

Polyamine	DP	Molecular Weight	Molecular Diameter*	Density at 25°	Nitrogen Content
Diethylenetriamine	2	103	7.0Å	0.95 g/cc	40.7%
Triethylenetetramine	3	146	7.8	0.97	38.3
Tetraethylenepentamine	4	189	8.5	0.99	37.0
Pentaethylenehexamine	5	232	9.0	1.01	36.2
Polyethyleneimine	14	600	12.3	1.03	33.4
"	116	5,000	24.7	1.04	33.0
"	700	30,000	44.9	1.05	33.0
"	1163	≈50,000	53.3	1.05	32.7
"	1745	≈75,000	61.0	1.06	33.0

*The molecular diameters of the amines were calculated using the formulas for the volume of a sphere ($V = 4.18\ r^3$) and literature values for their densities.

During this particular phase of the investigation a completely new method of trapping polyelectrolytes within microporous substrates was discovered. This is the so-called "Jack-in-the-Box" effect where a sudden expansion in the hydrodynamic volume of a polymer, triggered by pH (Table XI) causes it to be trapped against the sides of the containing pore.

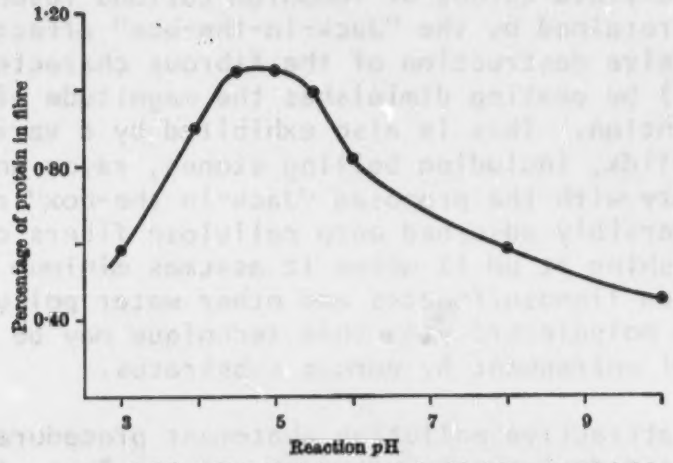
TABLE XI

Variation of Intrinsic Viscosity and Effective Molecular Volume of Polyethylenimine $\bar{M}n$=75,000, s.g. 1.2, with pH

pH	Intrinsic Viscosity	Effective Molecular Volume (Å 3)
12.5	1.00	1038
10.0	1.06	1100
7.0	1.85	1920
3.5	2.22	2303

This phenomenon is more conveniently and clearly demonstrated experimentally using proteins because their minimum hydrodynamic volume occurs at the isoelectric point, which is quite centrally located on the pH scale where the ionization of cellulose (pK=13.7) is relatively small.

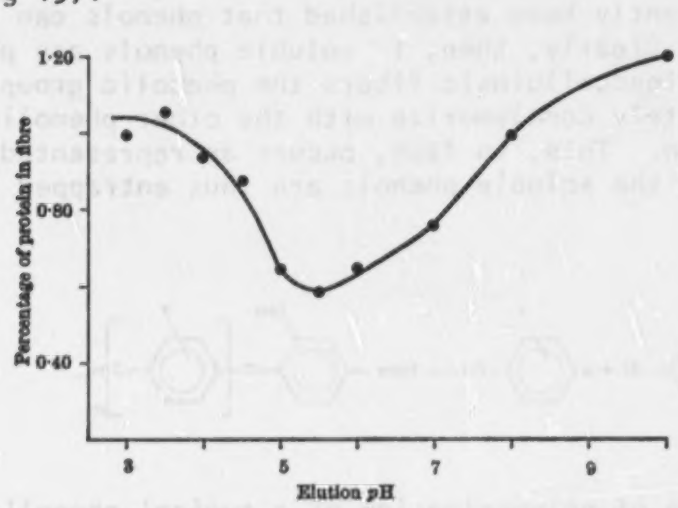
Thus, α-cellulose pulp fibers, impregnated with an aqueous solution of collagenous animal protein (Technical Protein Colloid No. 5V, Swift Chemical Co., Oak Brook, Illinois), give maximum retention of the protein at its isoelectric point (Fig 18) because the protein macromolcule is in its smallest form at this pH.



α-Cellulose fibre (5 g) impregnated with 0·08 per cent (w/v) aqueous protein solution (pH 3 to 10, 250 ml.) for 1 h and eluted with water (pH 7, 700 ml.) for 3 min.

Fig 18 shows the amount of protein retained by α-cellulose fiber after impregnation at various reaction pH's and elution with water at pH 7.

It is therefore capable of penetrating the largest number of the fiber pores. Conversely, if a series of protein-impregnated fibers are separately washed with water which has been adjusted to different pH values, maximum protein elution will be secured at the isoelectric point (Fig 19).



α-Cellulose fibre (5 g) impregnated with 0·08 per cent (w/v) aqueous protein solution (pH 5, 250 ml.) for 20 h and eluted with solution (pH 3 to 9, 700 ml.) for 3 min.

Fig 19 shows the amount of protein retained by α-cellulose fiber after impregnation at pH5 and elution at various pH's in the range pH3 - pH 10.

At this pH, the macromolecules within the fiber will have adopted their smallest and most elutable size. Above and below the isoelectric point, the protein macromolecule is distended by the mutual repulsions of its carboxylate anions or immonium cations respectively and it is therefore retained by the "Jack-in-the-box" effect. As anticipated, progressive destruction of the fibrous character (and the associated pores) by beating diminishes the magnitude of this type of polymer retention. This is also exhibited by a variety of other microporous solids, including boiling stones, rayon and cotton fibers. In conformity with the proposed "Jack-in-the-box" retention mechanism, PEI irreversibly adsorbed onto cellulose fibers can be readily eluted by washing at pH 12 where it assumes minimum hydrodynamic volume. Since lignosulfonates and other water pollutants such as proteins are polyelectrolytes this technique may be valuable for their nonchemical entrapment by porous substrates.

Another potentially attractive pollution abatement procedure emerged and was briefly scouted during this research grant. Thus, lignocellulosic fibers contain phenolic hydroxyl groups as an integral part of the fibers as depicted in Fig 20.

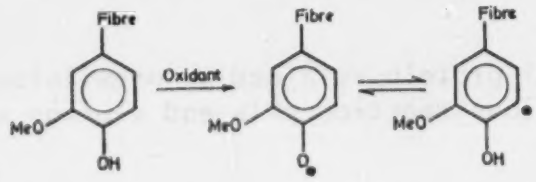


Fig 20 shows the process of formation and rearrangement of a free radical derived from a lignocellulosic fiber containing phenolic hydroxyl groups.

Moreover, it has recently been established that phenols can be oxidatively polymerized. Clearly, then, if soluble phenols are polymerized in the presence of lignocellulosic fibers the phenolic groups of the lignin should ultimately copolymerize with the other phenolic species in the polymerization. This, in fact, occurs as represented in Fig. 21 and Table XII and the soluble phenols are thus entrapped by the fibers.

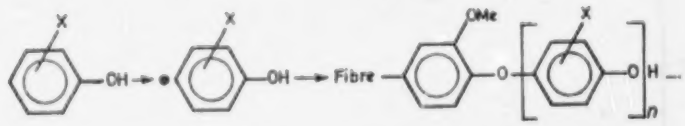


Fig 21 shows the mode of polymerization of a typical phenolic pollutant onto a lignocellulosic fiber containing phenolic hydroxyl groups (see Fig. 18).

TABLE XII

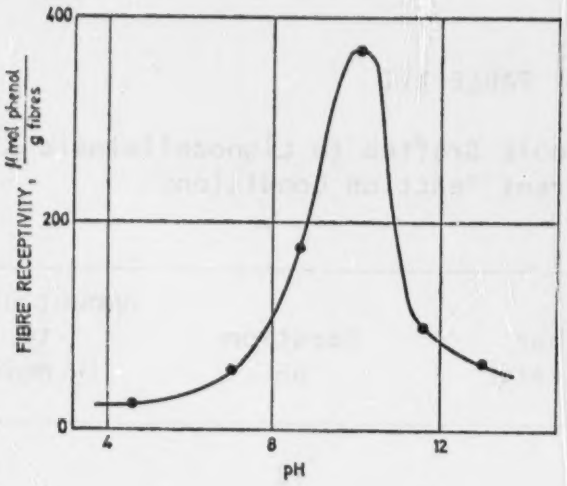
The Amounts of Various Phenols Grafted to Lignocellulosic Fibers Under Different Reaction Conditions

Phenol Grafted	Fiber Substrate	Reaction pH	Amount of Grafting to fibers (μ moles/g)
o-bromo-	a	12	55
	b	12	15
m-bromo-	a	12	27
	b	12	12
p-bromo-	a	12	80
	b	12	22
o-chloro-	a	10	400
2,6-dimethyl-	a	10	400

(a) unbleached kraft pulp of western red cedar and hemlock (85:15)

(b) Masonite-type Redwood fiber

This polymerization is noteworthy kinetically because no general termination step can be written and pollutants can theoretically be continued to be collected ad infinitum. The polymerization is induced by several oxidants including low cost ferric chloride and in a non-aqueous system, oxygen. It proceeds best at the pK value of the phenol (Fig. 22), and can be used to remove very small amounts of phenol from water solution.



Effect of pH on the amount of o-chlorophenol grafted to kraft pulp

Fig 22 shows the effect of pH upon the fiber receptivity during o-chlorophenol grafting, and indicates a maximum receptivity in the region of the pK_a of the phenol.

A more complex study has shown that both batchwise and columnar reactors are feasible, and that in the batchwise process, repetition of the whole reaction cycle increases the pollutant grafted almost linearly with the number of reaction cycles (Fig. 23).

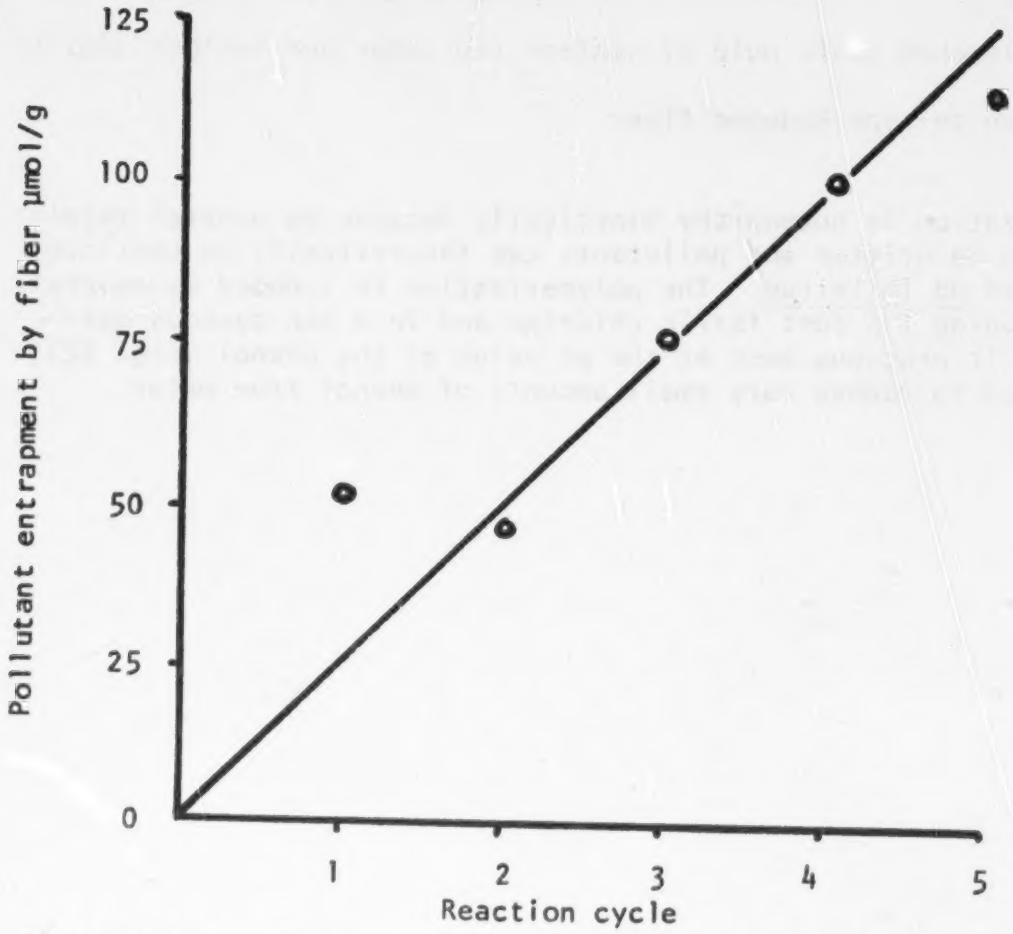


Fig. 23 shows the entrapment of o-Bromophenol by kraft pulp. The column process as a model for a continuous system used o-halophenols as pollutants and potassium ferricyanide as oxidant. Table XIII shows that, as expected, the collection efficiency is a maximum at the top of the column.

TABLE XIII

Continuous Entrapment of Model Pollutant (o-Chlorophenol) by Column of Kraft Pulp

Column Temperature	Pollution Entrapment by Fiber at Top of Column	at Bottom of Column
25°C	122 μ mol/g	75 μ mol/g
55 "	158 "	54 "

A more extensive study of the chemistry of this copolymerization technique has also been made. In this, the relative reactivity of the isomeric halophenols has been determined, and the efficiency of various oxidizing agents has been evaluated. Proof that copolymerization is indeed occurring onto the lignin in the fiber rather than homopolymerization in solution, is obtained by the difference in receptivities of Masonite and α-cellulose fibers (Fig. 24).

Extraction of both these grafted fibers with dichloromethane showed that phenolic material in the α-cellulose, while present, was not firmly attached and is probably only physically entangled within the fiber matrix. Table XIV shows results obtained using various halophenols and oxidants.

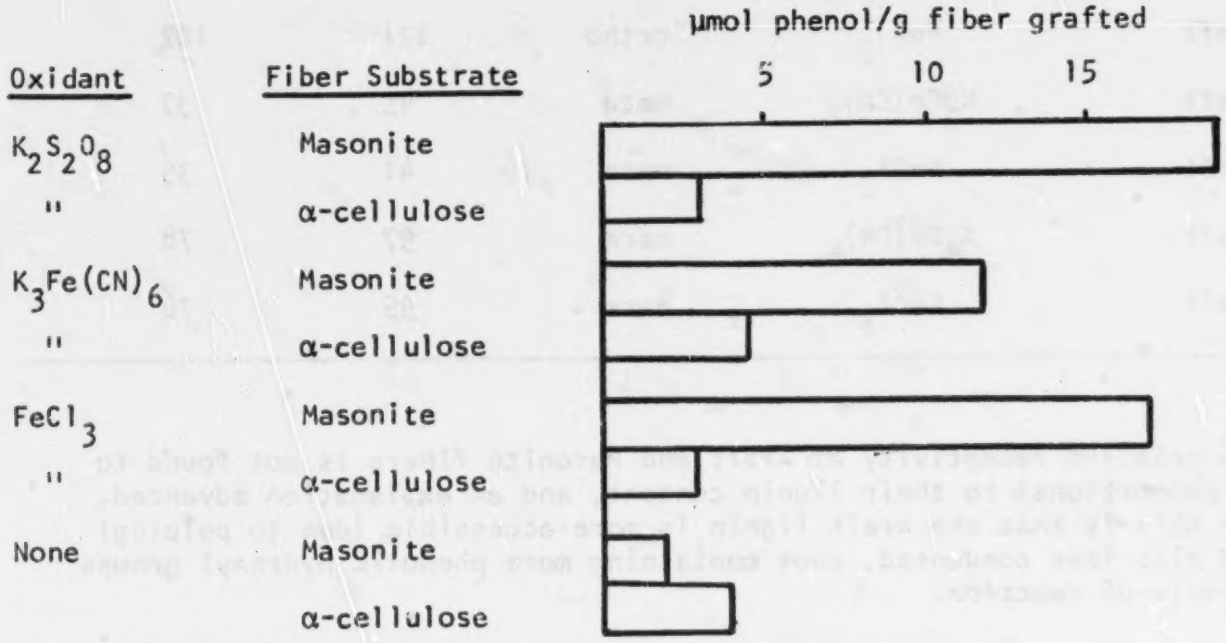


Fig 24 o-Bromophenol receptivity of α-cellulose Masonite-type fibers.

TABLE XIV

Effect of Dichloromethane Extraction on the Bromophenol Content of Fibers

Fiber Substrate	Oxidant System	Bromophenol Grafted	Phenol receptivity of fiber μ mol phenol/g fibers	
			Unextracted	Extracted
α-Cellulose	None	ortho	4.1	1.1
α-Cellulose	$K_3Fe(CN)_6$	ortho	4.9	4.7
Masonite	None	ortho	1.2	0.7
Masonite	$K_3Fe(CN)_6$	ortho	16.8	15.3
Kraft	None	ortho	0.3	0.5
Kraft	$K_3Fe(CN)_6$	ortho	11.3	11.2
Kraft	$K_2S_2O_8$-$FeSO_4$	ortho	20.7	20.8
Kraft	$FeCl_3$	ortho	9.5	10.0
Kraft	$K_3Fe(CN)_6$	ortho	107	82
Kraft	$FeCl_3$	ortho	121	102
Kraft	$K_3Fe(CN)_6$	meta	45	37
Kraft	$FeCl_3$	meta	41	35
Kraft	$K_3Fe(CN)_6$	para	97	78
Kraft	$FeCl_3$	para	95	76

The relative receptivity of kraft and Masonite fibers is not found to be proportional to their lignin content, and an explanation advanced for this is that the kraft lignin is more accessible (due to pulping) and also less condensed, thus containing more phenolic hydroxyl groups capable of reaction.

Studies as yet incomplete indicate that low molecular weight lignin fractions can be coupled to groundwood fibers using reaction conditions similar to the above.

The benefits to be anticipated from this system are demonstrated by

Fig. 25 which summarizes the improvements obtained in the tensile strength of unbleached kraft sheets by the grafting of pulp wastes.

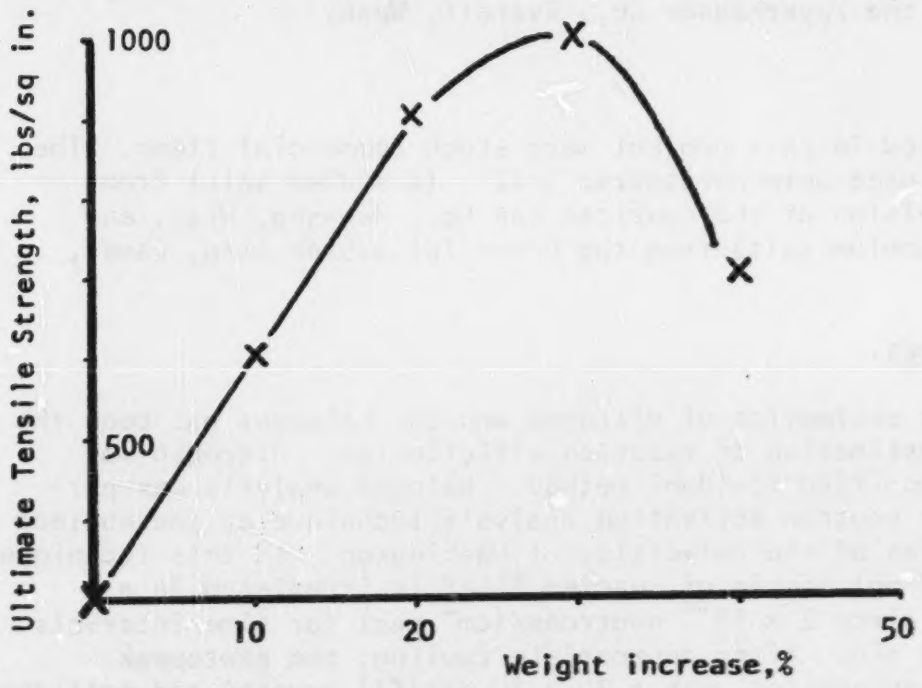


Fig 25 shows the increase in ultimate tensile strength in pounds per square inch with the amount of pulp waste pollutant grafted to the sheet.

EXPERIMENTAL SECTION

Materials.

Cellulosic fibers used comprised: a slightly beaten α-cellulose (Whatman No. 1 filter paper, W & R Balston Ltd, England). Cotton, uncut and cut to 3 mm lengths, from the Red Cross Cotton Co., Johnson and Johnson, New Brunswick, N. J. A commercial unbeaten α-cellulose (Pulp-S-947, Rayonier Corp., Shelton, Washington.).

Lignocellulosic fibers comprised: glassine, containing 0.6% lignin, was Powder paper #3, distributed by Eli Lilly & Co. and the product of St. Regis Paper, Rhinelander, Wisc. Asplund Wood Fibers from: (a) white fir (Abies concolor), (b) western hemlock (Tsuga heterophylla), (c) red gum (Liquidambar styraciflua). Asplund pulp fibers (85% yield) from a neutral sulfite semi-chemical treatment of an 80:20 mixture of western red alder (Alnus rubra, Bong) and cottonwood, (Populus deltoides). Masonite fibers from redwood (Sequoia sempervirens) and a 70:30 mixture of Douglas fir (Pseudotsuga taxifolia) and Ponderosa pine (Pinus ponderosa). Douglas fir bark fibers containing 38 and 25.6% lignin (WEF 303 and 608). An unbleached kraft pulp

containing 8.2% lignin derived from an 85:15 mixture of western red cedar (Thuja plicata) and western hemlock (Tsuga heterophylla), donated by the Weyerhauser Co., Everett, Wash. A dry, unbleached, unbeaten sulfite pulp containing 12% hemicelluloses and 1.3% lignin, also donated by the Weyerhauser Co., Everett, Wash.

Chemicals.

All chemicals used in this project were stock commercial items. The lignosulfonates used were Marasperse N-22 , (a sodium salt) from the Marathon Division of the American Can Co., Menasha, Wisc, and Orzan A, (an ammonium salt) from the Crown Zellerbach Corp, Camas, Wash.

Analytical Methods.

In this work the estimation of nitrogen and the halogens has been the main method of estimation of reaction efficiencies. Nitrogen was estimated by a modified Kjeldahl method. Halogen analysis was performed using the neutron activation analysis technique at the Nuclear Reactor facilities of the University of Washington. In this technique a small (100-500 mg) sample of reacted fiber is irradiated in a neutron flux of circa 2×10^{12} neutrons/(cm^2 sec) for time intervals between 5 and 30 min. After appropriate cooling, the photopeak of the halogen was counted with a 3" x 3" NaI(Tl) crystal and multichannel analyser. Spectrum stripping was occasionally necessary to eliminate the interference encountered from both sodium and other metal ions present in trace amounts. Sulfur analysis was performed similarly using the same conditions, but encounters more interference from sodium in the sample, and for this reason exchange of lithium for sodium by elutriation of the sample with a solution of a soluble lithium salt prior to analysis has been found to be desirable when only small amounts of sulfur are present.

Reaction of Pulp Fibers with Fiber Reactive Dye.

A stirred suspension of fiber (4.55 g) in distilled water (177.5 g) at 25° having a consistency of 2.5% was treated with the fiber reactive dye. After the dye had dissolved, sodium chloride (4.55 g) was added and the mixture was stirred for 15 min and adjusted to pH 10.50 using a 10% sodium carbonate solution. Stirring was then continued for 90 min when the pH had dropped to 10.35. The fibers were collected by filtration on a foraminous plate, washed with hot distilled water (80°, 400 ml) for 70-90 min, refiltered and rewashed with hot distilled water (80°, 400 ml) and again soaked in hot distilled water (80°, 400 ml) for 70-90 min. Finally the fiber mass was again filtered off and washed with cold distilled water until the volume of the combined washings was 2000 ml.

In addition to analysis for nitrogen and chlorine by Kjeldahl and neutron activation methods, a check on the amount of dye unreacted was made by UV spectrophotometry using the dye absorption maximum at 3600 Å.

Reaction of Wood and Bark Fibers with Fiber Reactive Dye.

A stirred suspension of fiber (5g) in distilled water (200 ml) at 26° was treated with the fiber reactive dye (1) and after 15 min sodium chloride (5g) was added. Stirring was then continued for 15 min when the mixture was adjusted to pH 10.50 using solid sodium carbonate for the Asplund fibers and a 10% sodium carbonate solution for the Masonite and bark fibers. During the following reaction period (90 min) the pH was kept constant by the addition of more of the same alkaline reagent. The fibers were then collected by filtration on a foraminous plate, washed with distilled water (26°, 1800 ml for the Asplund fibers, 900 ml for the Masonite and bark fibers), resuspended and soaked in distilled water (26°, 500 ml) overnight, refiltered and washed until the volume of the combined washings was either 3000 ml (Asplund fibers) or 2000 ml (Masonite and bark fibers).

Reaction of Dyed Fibers with Phenols or Thiophenols.

The reaction between dyed fibers and the phenols or thiophenols was carried out by adding dyed redwood Masonite fibers (2.2g) to a stirred solution of the phenol or thiophenol (1 mmol) in distilled water (80 ml) at 26°. The pH of the suspension was adjusted to and maintained at 11.0 for 2.5 hr using a 0.1N sodium hydroxide solution, when the fibers were collected by filtration and washed with distilled water (26°, 1000 ml). The amount of unreacted dye was again determined by UV spectrophotometry.

Reaction of Cyanuric Chloride with Model Phenols.

2,4,6-Tri-(4-sec-amylphenoxy)-s-triazine. A solution of cyanuric chloride (3.69g, 0.02 mol) in acetone (100 ml) or dioxan (50 ml) was added with vigorous stirring to ice-water (200 ml). The resultant finely divided suspension, maintained at 0-5°, was then treated dropwise with a sodium hydroxide (2.4g, 0.06 mol) solution (200 ml) of 4-sec-amylphenol (9.85g, 0.06 mol) added over 15 min. The mixture was stirred for 2 hr at the same temperature and then for a further hour at room temperature. The crystalline solid which had separated was collected, washed well with water and then with methanol. Subsequent crystallization from methanol-ethyl acetate yielded the product characterized in Table II. The other eighteen compounds listed in Table II were prepared similarly. Chlorine and nitrogen analyses were carried out as previously described.

Augmentation of Lignosulfonate Molecular Weight.

Condensation of lignosulfonates with formaldehyde were typically carried out by refluxing a solution of the dialysed or undialysed lignosulfonate (8g) in water (150 ml) for 11-60 hr with an aqueous formaldehyde solution (37%, 2 ml) and concentrated (d, 1.84) sulfuric acid (4 ml). Sample withdrawal and the further addition of aqueous formaldehyde (37%, 2-6 ml) were made intermittently.

Dialyses were carried out over a period of days using seamless cellophane tubing (100 ml capacity, 3.8 cm diam) immersed in constantly circulating water (18.1). Molecular weight changes were followed by intrinsic viscosity measurements made on lignosulfonate solutions in 0.1M sodium chloride at 25 ± 0.5°C using a Fenske viscometer.

Coupling of Lignosulfonates with Cyanuric Chloride.

Cyanuric chloride (1g) partially dissolved in dioxan (10 ml), was slowly added dropwise to a solution (55 ml) of dialysed sodium lignosulfonate (17g/dl, $[\eta]$=0.051 dl/g) at pH 9.1 and <5° with vigorous stirring. As the cyanuric chloride was added, the viscosity of the solution increased gradually initially and then dramatically until the lignosulfonate almost became insoluble. When this point was reached, the solution was diluted with water to prevent the larger molecular weight lignosulfonates from becoming totally insoluble. This dilution was carried out when the solution became so viscous that the stirrer would no longer mix the solution of polymerizing lignosulfonates. Caution in dilution was required because too great a dilution caused the polymerization reaction to slow down perceptibly. In addition, the more dilute the lignosulfonate solution, the larger the amount of cyanuric chloride consumed to achieve an equal molecular weight gain. The solution became viscous and was diluted several times before the reaction was complete. The reaction was considered complete when no further thickening of the solution occurred, irrespective of how much cyanuric chloride was subsequently added. The pH was maintained above 9.0 with 5N NaOH throughout the reaction. After centrifuging off the precipitated lignosulfonates, the soluble fraction was dialysed for four days. By either adding less cyanuric chloride or by extracting samples at intermediate points during the reaction, a range in molecular weights similar to the formaldehyde condensed lignosulfonates was obtained.

Oxidative Complexing of Lignosulfonates with Dichromate.

Acetic acid (11.4 ml) was added to a solution (189 ml, 6.5g/dl) at room temperature of dialysed sodium lignosulfonate ($[\eta]$=0.051 dl/g) with stirring. $Na_2Cr_4O_7 \cdot 2H_2O$ (7.5g) was then added. Samples (25 ml) were then removed every 10 min for 1 hr, and diluted with water (300 ml) to stop the polymerization, neutralized with 5N NaOH, and dialysed for 7 days in a similar manner to the cyanuric chloride samples. After 25 min, a noticeable thickening of the solution occurred. In order to prevent precipitation of the lignosulfonates in solution, water (50 ml) was added.

Oxidative Coupling of Lignosulfonates.

A solution (200 ml, 6.5g/dl) at room temperature of dialysed sodium lignosulfonate ($[\eta]$=0.051 dl/g) was adjusted to pH 10 with 5N NaOH. $K_3Fe(CN)_6$ (14g) was then added and the pH was maintained above 10 with 5N NaOH throughout the reaction. Samples (25 ml) were taken

intermittently, diluted with water (175 ml), the pH adjusted to 3.5 to stop the reaction, and dialysed for 7 days in a similar manner as before.

Reaction of Cyanuric Chloride with Kraft Fibers.

Two reaction procedures designated A and B were employed.

Procedure A: A vigorously stirred suspension of kraft fibers (5g) in a water-acetone mixture (1:1, 200 ml) at -10° was treated with a solution of cyanuric chloride (2g) in acetone (50 ml) and then adjusted to pH 12 with an aqueous 5N sodium hydroxide solution. After stirring for 10 min, the fibers were collected by filtration on a foraminous plate, sequentially washed with water (200 ml), acetone (300 ml) and dioxan (150 ml) extracted with dioxan for 2 hr in a Soxhlet apparatus, dried at 100°, and analyzed for nitrogen and chlorine.

Procedure B: A vigorously stirred and cooled suspension of kraft fibers (5g) in water (100 ml) and acetone (100 ml) at -10° was treated with a solution of cyanuric chloride (2g) in acetone (50 ml). When the temperature of the fiber suspension was again -10° an aqueous 1N solution of sodium hydroxide (15 ml) was added dropwise during 2 min and after 3 min more the pH was lowered to ∿4 by the addition of dilute sulfuric acid, thereby terminating the reaction. The fibers were collected as before, washed successively with water (2000 ml) and acetone (400 ml) soaked in acetone for 24 hr, filtered, rewashed with acetone (200 ml), dried at room temperature under reduced pressure, and analyzed for nitrogen and chlorine.

Rate of Hydrolysis of Cyanuric Chloride.

A solution of cyanuric chloride (1g) in acetone (50 ml) was added to a vigorously stirred mixture of water (100 ml) and acetone (100 ml) at -10° and a 1N solution of aqueous sodium hydroxide was used to adjust and maintain the mixture at pH 10. The consumption of the sodium hydroxide was observed as a function of time and was used to calculate the extent of hydrolysis of the cyanuric chloride.

Reaction of Dyed Kraft Fiber with Amino Compounds.

The amino compound (500 mg) was added to a stirred suspension of the dyed kraft fibers (5g) in water (200 ml) at 25°. The pH was adjusted to selected values with 0.1N sulfuric acid or 0.1N sodium hydroxide, and after a 2 hr reaction period, the fibers were collected by filtration and washed sequentially with dilute sulfuric acid (pH 2.5, 300 ml) sodium hydroxide solution (pH 11, 300 ml), and distilled water (300 ml). This washing was repeated twice, followed by elutriation of the fibers with distilled water to a total filtrate volume of 3000 ml. Control dyed fibers were treated similarly without any addition of amine.

Batch Reactions.

A suspension of fiber (2g) in distilled water (78g) at 25° was stirred with the oxidizing agent for 30 min. The halophenol in acetone (5 ml) was then added and stirring was continued for 120 min. Each of the three isomeric bromophenols was used at two levels in combination with the three oxidants, potassium persulfate-ferrous sulfate, alkaline potassium ferricyanide and ferric chloride as follows: (a) bromophenol (6.8 mmol), acetic acid (6 ml), potassium persulfate (2.4g) and ferrous sulfate (20 mg), (b) bromophenol (18.68 mmol), acetic acid (12 ml), potassium persulfate (4.8g) and ferrous sulfate (20 mg), (c) bromophenol (6.84 mmol), potassium ferricyanide (1.820g) and sodium hydroxide (440 mg), (d) bromophenol (13.68 mmol), potassium ferricyanide (3.64g) and sodium hydroxide (880 mg), (e) bromophenol (6.84 mmol) and ferric chloride (1g). Control experiments (f) were also carried out in which the oxidants were omitted and only the bromophenol (6.84 mmol) was included with the fibers.

The fibers were collected by filtration on a foraminous plate, washed consecutively with distilled water (200 ml), hydrochloric acid (0.1M, 700 ml), aqueous sodium hydroxide (0.1M, 700 ml), distilled water (700 ml) and acetone (200 ml). The washed fibers were dried at 60°.

The effect of pH on the receptivity of the fiber was studied only in the case of o-chlorophenol oxidatively coupled using potassium ferricyanide. The fibers were stirred with the oxidizing agent (4.6g) for 30 min at 25°. A solution of o-chlorophenol (6.56 mmol) in ethanol (10 ml) was then added dropwise over 180 min. The pH was adjusted using 5N sulfuric acid or 5N sodium hydroxide. The washing and drying procedures were unchanged.

Batch Entrapment of Phenolic Pollutants by Lignocellulosic Fibers.

A suspension of the lignocellulosic fiber (2g) in distilled water (78g) at 25° was stirred with the oxidizing agent [$K_3Fe(CN)_6$, 1.82g; NaOH, 0.44g] for 30 min and then treated with a solution of the model pollutant (o-bromophenol, 1.2g, 6.84 mmol) in acetone (5 ml). After stirring for 2 hr the fibers were collected by filtration, washed sequentially with distilled water (500 ml), dilute aqueous hydrochloric acid solution (0.1N, 200 ml), dilute aqueous sodium hydroxide solution (0.1N, 200 ml), distilled water (500 ml) and acetone (200 ml), dried at 60°, subjected to neutron activation analysis and found to contain o-bromophenol (80 μmol/g). Repetition of the foregoing procedure using the same fibers gave the increased entrapment of pollutant with each reaction cycle summarized in Fig. 23.

Continuous Entrapment of Phenolic Pollutants by Lignocellulosic Fibers.

Solutions of the model pollutant (o-chlorophenol, 0.85g, 6.56 mmol) in distilled water (1400 ml) and potassium ferricyanide (4.6g), in

distilled water (1400 ml) adjusted to pH 10 with sodium hydroxide, were simultaneously added dropwise to the top of a column (2.5 x 14 cm) of a kraft fiber (2g) suspension (consistency, 5.61%) in water and allowed to percolate downwards and through during a period of 40 hr. The fibers were then extruded from the column and divided into two equal fractions corresponding to the top and bottom halves of the column before application of the washing, drying and analytical procedures detailed for the batch entrapment experiments. The results obtained are collected in Table XII.

Reaction of Cyanuric Chloride Treated Fibers with Pentaerythritol Tetra(3-mercaptopropionate).

Due to the ease of oxidation of thiols in basic media, this thiol grafting reaction was conducted in a nitrogen atmosphere. To a cooled and stirred suspension of cyanuric chloride treated α-cellulose (1g) in acetone (100 ml) at 0° was added pentaerythritol tetra (3-mercaptopropionate) (0.29g, 0.6 mmol). After 30 min stirring, sufficient 1N sodium hydroxide (2.4 ml) to ionize all the thiol groups in the thiol compound was added dropwise via a hypodermic syringe. After a further 30 min the flask was allowed to warm to ambient temperature, and after 1 hr the fibers were collected on a foraminous plate and washed successively with acetone (200 ml).

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84-116 The reaction of lignin model compounds with cyanuric chloride.

117-163 The increase in molecular weight of lignosulfonates by condensation with formaldehyde and the uses of the products.

163-186 The reaction of cyanuric chloride with lignocellulosic fibers and the effects of various reaction conditions.

187-207 The reaction of fiber reactive dye treated lignocellulosic fibers with amines.

208-217 The oxidative coupling reaction of chlorophenols and kraft pulp.

218-233 The mechanism of polyethylenimine retention by porous materials.

233-263 The oxidative coupling of phenolic pollutant model compounds to lignocellulosic fibers.

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LIST OF PATENTS AND PUBLICATIONS

Although a number of findings believed to be patentable have been made during this work, the necessary complete reduction to practice is not yet concluded.

The following publications have been produced as a result of this project.

Allan, G. G., Mauranen, P., Desert, M. D. and Reif, W. M., *Paperi Puu, 50*:529 (1968).

Allan, G. G., Lacitis, A., Lui, F-m., Lee, J-h. and Mauranen, P., *Holzforschung 23*:198 (1969).

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1 Accession Number	2 Subject Field & Group	SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM
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27 Abstract

Laboratory studies were conducted to determine if the collection of pollutants from water using fibers was a feasible concept. Any cellulosic or lignocellulosic fibers can be reacted with di- or tri-halogeno-s-triazines in simple aqueous conditions so that about 10% by weight of reactive sites can be built into the fiber. The modified fibers can be regarded as polychloro-s-triazinylated fibers in which each s-triazine ring contains approximately one or two reactive chlorine atoms. The extent of reaction is generally determined by the stereotopochemistry of the fiber and in particular by its lignin content and its microporous structure. Chloro-s-triazines are capable of reacting in aqueous solutions with amines, mercaptans and phenols, typical of those present in pulping wastes and bleach plant effluent. The efficiency of this system is obviously increased as the size of the pollutant removed per reactive fiber size is increased. Methods to increase the size of lignosulfonates by condensation have therefore been developed.

Two new methods for the collection of pollutants by fibers based on oxidative grafting and physical entrapment by hydrodynamic volume changes have also been discovered and a procedure for the characterization of copolymer compositions by surface tension has been established.

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